On the question of ferromagnetism in alkali metal thin films

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Electronic and magnetic structure of (100) films of K and Cs are calculated within the plane-wave projector augmented wave (PAW) formalism of the density functional theory (DFT) using both local spin density approximation (LSDA) and the PW91 generalized gradient approximation (GGA). Only a 6 layer Cs film is found to have a ferromagnetic (FM) state which is degenerate with a paramagnetic (PM) state within the accuracy of these calculations. This is at variance with the results obtained from a finite thickness uniform jellium model (UJM). Implications of these results for the experiments on transition metal doped alkali metal thin films and bulk hosts are discussed.

I. INTRODUCTION

Bulk and thin films of alkali metals containing $3d$ transition metal (TM) impurities have been studied experimentally for quite some time now[1,2,3,4,5]. The most intriguing property of these systems is the large magnetic moment they posses. Beckmann and Bergmann[3], through anomalous Hall measurements, show that a Co impurity on a Cs film has a (total) magnetic moment as large as 9 μ_B, and that in bulk Cs has a moment of 8 μ_B. An Fe impurity has a moment of 7 μ_B both on a Cs film, and inside bulk Cs. Bergmann and Song[5] predicted large moments in V doped alkali metals which ranged from 6-7 μ_B in a Na host to 4 μ_B in a Cs host. Nearly two decades ago, Riegel *et al.*[1] and Kowallik *et al.*[2], through magnetic susceptibility measurements, showed that Fe and Ni impurities in K, Rb and Cs hosts have large magnetic moments. Gambardella *et al.*[4] in their X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements find total magnetic moments of 6.63 μ_B, 5.59 μ_B, and 3.55 μ_B respectively for Fe, Co and Ni impurities on K films.

These startling findings raise the obvious question of the origin of such large magnetic moments. And that is where opinions differ. Riegel and co-workers[1] argued that the TM atoms remain isolated inside an alkali host due to the latter's rather large lattice constant. This isolated nature of the TM atoms retain their atomic spin and orbital moments, which are, otherwise, quenched in a solid environment due to hybridization and crystal-field effects. The moments are, therefore, essentially those of isolated TM atoms. Gambardella *et al.*[4] also subscribe to this view. Comparing their observed XAS spectra with the calculated ones, they show that the TM atoms are indeed in their atomic configurations. Beckmann and Bergmann[3] and Bergmann and Song[5], on the other hand have argued that the only way to explain the observed moments in the TM-alkali metal systems is to assume that the electrons in the alkali host are polarized in presence of the TM atoms. This is exactly how an Fe impurity behaves in a Pd host, where it polarizes the Pd electrons leading to a giant moment[6,7].

TM-alkali metal systems have been studied theoretically also. And the picture that emerges supports Riegel *et al.* and Gambardella *et al.*'s views. Through local density approximation (LDA) plus local Coulomb energy (U) calculations within the density functional (DFT) theory, Kwon and Min[8] have shown that an Fe impurity behaves differently in a Cs host compared to a Pd host. There is no polarization of the Cs electrons, rather the Fe impurity remains isolated leading to atomic-like large moments. Sahu and Kleinman[9] performed DFT calculations for V impurities in bulk Na, and Co in Na and K. They also rejected the hypothesis that polarization of the host electrons is responsible for the observed moment.

In support of their proposition, Bergmann and co-workers cited Okazaki and Teraoka's[10] work. In this, the authors use a uniform jellium model (UJM) of finite thickness to study electronic and magnetic properties of alkali metal thin films. Using local spin density approximation (LSDA) for the exchange-correlation functional, they find that depending on the electron density ρ_0 (equivalently $r_s = (3/4\pi\rho_0)^{1/3}$), the UJM can have a ferromagnetic ground state in certain ranges of thickness (D). In a later detailed work[11], they show that for $r_s = 6$, paramagnetic (PM) and fully polarized ferromagnetic (FPF) solutions exist at every thickness. They also find partially polarized ferromagnetic (PPF) solutions for $11.9 \leq D \leq 18.48$, and $22.2 \leq D \leq 27.6$ Bohr, and antiferromagnetic (AF) solutions for $11.5 \leq D \leq 15.0$ Bohr. The ground state of the system turns out to be FPF at $D \leq 9$ Bohr, PM for $9 \leq D \leq 11.9$ Bohr, PPF at $11.9 \leq D \leq 12.8$ Bohr, FPF at $12.8 \leq D \leq 16.4$ Bohr, PPF at $16.4 \leq D \leq 17.1$ Bohr, PM for $17.1 \leq D \leq 22.1$ Bohr, PPF at $22.1 \leq D \leq 25.6$ Bohr, and PM at $25.6 < D$ Bohr. Based on these results, very thin films of Cs and Rb are expected to be ferromagnetic[10].

In order to throw further light on this debate, it becomes crucial to understand the electronic and magnetic structures of specific alkali metal thin films through first-principles atomistic calculations (as opposed to the UJM). In particular, one needs to address the question: are thin films of alkali metals, in particular Cs, really ferromagnetic? For this purpose, I have done DFT calculations for K and Cs thin films using both LSDA and GGA. The main results in this brief report are: for most thicknesses, alkali metal thin films do not have a FM state; only a 6 layer Cs film

has a FM state, which, however, is degenerate with the PM state. The numerical methods employed and the results obtained are discussed in detail in the next two sections.

II. METHOD

Calculations were performed within the framework of DFT. VASP[12,13,14,15] was used for all the calculations. The wave functions are expressed in a plane wave basis set with an energy cutoff of 400 eV. The Brillouin zone integrations are performed using the Monkhorst-Pack scheme. Ionic potentials are represented by PAW. Both LSDA and PW91 GGA functionals are used for the exchange-correlation energy. The preconditioned conjugate gradient method as implemented in VASP is used for wave function optimization, and the conjugate gradient is used for ionic relaxation. K(100) and Cs(100) thin films are represented by a repeated slab geometry. Each slab contains the desired number of (100) planes of the alkali metal. In the starting geometry, the atoms in the films were placed at their bulk positions. Values of the bulk lattice constant used were calculated with the particular method (LDA or GGA) in use. For the bcc bulk K, the lattice constants obtained were 5.04 Å and 5.28 Å respectively using LDA and GGA. For bcc Cs, the corresponding values turned out to be 5.77 Å and 6.13 Å respectively. The experimental lattice constants for K and Cs are 5.23 Å and 6.05 Å respectively. Consecutive slabs were separated by a vacuum space equal to 6 atomic layers. For 1, 2 and 3 layer films, a (2×2) surface supercell was used. However, there were no forces on any of the atoms along the (100) planes. Therefore, for thicker films, a (1×1) surface supercell was used to reduce computational cost. Only one of the atoms in the supercell was held fixed, and all other atoms were allowed relax freely in all three directions without any symmetry constraints. As already mentioned, there were no forces, and hence no movement of the atoms in the (100) planes. Relaxation perpendicular to the (100) planes were also rather small. A $(6 \times 6 \times 1)$ k-point mesh was used for (2×2) surface supercell, while for the (1×1) surface supercell, a $(8 \times 8 \times 1)$ k-point mesh was used. Absolute convergence of energy with respect to energy cutoff and the number of k points was thoroughly tested. Similar methods were used earlier to study thin Al(110) films by Ciraci and Batra[16].

III. RESULTS

Calculations were done for 3, 5 and 7 layer K films, and for Cs films having thicknesses from 1 to 7 atomic layers. I searched for both paramagnetic and ferromagnetic (FM) solutions for both K and Cs films at each thickness. I do not consider AFM states, since ref.[10] and [11] do not find an AFM ground state at any thickness. While searching for a FM state, the initial Hamiltonian was set up with a spin moment of 2 μ_B on each atom. In almost all cases the films converged to PM states with zero or a vanishingly small moment (which is probably a remanent of the initial Hamiltonian). The only exception was a 6 layer Cs film for which a small moment of ~ 0.1 μ_B per atom was found in both LSDA and GGA. In order to be convinced that it is, in fact, a ferromagnetic state, I plot the band structures and the electronic densities of states (DOS) in Figure. 1 for a 6 layer Cs film. As is clearly seen, the minority (down) spin bands are slightly shifted up in energy compared to the majority (up) spin bands. This is reflected in the DOS as well. It should also be noted that I obtain a staircase-like DOS expected for a quasi-two dimensional system of electrons, as discussed in detail in Ref.[16]. Since in all films except a 6 layer film of Cs, the initial FM films converge to a PM state, the energies in the two states are the same. This and other results are listed in Tables I to IV. The binding energy per atom for an N atom film given in these tables are defined as follows.

$$BE = \frac{1}{N}\left(NE_A - E(\text{film})\right), \tag{1}$$

where E_A is the energy of an isolated alkali metal atom, and E(film) is the total energy of a film containing N alkali metal atoms. Interestingly, even in 6 layer Cs films, the energies of the PM and FM states are identical in LSDA, and differs by only 1 meV per atom in GGA. This energy difference, however, is at the limit of accuracy of the present DFT based methods. Therefore, we can only claim that a 6 layer Cs film has degenerate PM and FM ground states.

While K-films are not expected to be ferromagnetic, as one requires thinner films for metals with smaller r_s to find a FM state according to ref.[11], I do not find any (unique) FM ground state for Cs films either. In fact, I do not even find a FM state except for a 6 layer Cs film. A few points are in order here. 1. In the finite-thickness UJM that Okazaki and Teraoka have considered, thickness is a continuous variable, but for a real metal film, it can only take discrete values determined by the number of atomic layers in the film. Comparing with the LSDA results of ref.[10], Cs films with 2 layers (thickness of 3.21 Å = 6.07 Bohr) and 4 layers (thickness 8.93 Å = 16.88 Bohr) are expected to be FPF and PPF respectively. However, both these are found to be paramagnetic in my calculations. A 6 layer film (thickness 14.63 Å = 27.66 Bohr) is found to have a FM state, albeit with a small moment, while a finite thickness UJM is expected to be PM beyond a thickness of 25.6 Bohr. 2. Even in Okazaki and Teraoka's calculations[10,11],

TABLE I: Thickness (Å) and binding energy (BE, eV/atom) of K(100) films containing specified number of atomic layers. Results for PM(FM) states are obtained using LDA(LSDA).

No. of layers	PM		FM	
	thickness	BE	thickness	BE
3	5.04	1.007	5.04	1.007
5	10.04	1.066	9.94	1.066
7	15.17	1.091	15.15	1.091

TABLE II: Thickness (Å) and binding energy (BE, eV/atom) of K(100) films containing specified number of atomic layers. Results for both PM and FM states are obtained using PW91 GGA.

No. of layers	PM		FM	
	thickness	BE	thickness	BE
3	5.28	0.911	5.27	0.911
5	10.57	0.961	10.56	0.961
7	15.85	0.982	15.84	0.982

the energy difference between a PM and a FM state is rather small, ∼mev (Fig. 4 of Ref.[10]). Their calculations are also based on the local density and local spin density approximations of the DFT. Therefore, it would be difficult to argue in favor of a FM ground state on the basis of those calculations, though, admittedly, they found a definite trend at $D = 7$ and 8 with varying r_s. 3. The present calculations also bring out the importance of doing an atomistic first-principles calculation, the results of which differ significantly from those of a model system studied in refs.[10,11].

IV. CONCLUSIONS

In conclusion, through first-principles atomistic calculation using plane-wave PAW formalism within LSDA and GGA of the DFT, I show that neither K nor Cs films can be claimed to have a (unique) FM ground state within the accuracy of these calculations. Only a 6 layer Cs film has a FM ground state, but that is degenerate with a PM state. Present work points out that there are crucial differences in the behavior of a UJM and a real atomistic system. More accurate calculations, such as quantum Monte Carlo, may be required to resolve the issue of ferromagnetism in alkali metal thin films. I would like to end by pointing out that these results, by themselves, do not rule out the possibility of polarization of electrons in an alkali metal film in presence of TM impurities (though that also has been argued against in refs.[8] and [9]), but definitely show that within LSDA and GGA, one cannot claim alkali metal thin films to have a FM ground state.

V. ACKNOWLEDGMENTS

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TABLE III: Thickness (Å), binding energy (BE, eV/atom) in the PM and FM states, and magnetization (M, μ_B per atom) in the FM state of Cs(100) films containing specified number of atomic layers. Results are obtained using LDA/LSDA.

No. of layers	PM		FM		
	thickness	BE	thickness	BE	M
1	–	0.580	–	0.580	0.0
2	3.21	0.779	3.18	0.779	0.0
3	5.98	0.853	5.93	0.853	0.0
4	8.93	0.884	8.91	0.884	0.0
5	11.56	0.908	11.56	0.908	0.0
6	14.63	0.919	14.61	0.919	0.1
7	17.42	0.929	17.42	0.929	0.0

TABLE IV: Thickness (Å), binding energy (BE, eV/atom) in the PM and FM states, and magnetization (M, μ_B per atom) in the FM state of Cs(100) films containing specified number of atomic layers. Results are obtained using PW91 GGA.

No. of layers	NM		FM		
	thickness	BE	thickness	BE	M
1	–	0.511	–	0.511	0.0
2	3.07	0.686	3.07	0.686	0.0
3	6.13	0.752	6.13	0.752	0.0
4	9.25	0.774	9.24	0.774	0.0
5	12.30	0.794	12.31	0.794	0.0
6	15.36	0.800	15.33	0.801	0.1
7	18.34	0.810	18.38	0.810	0.0

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Figure Captions

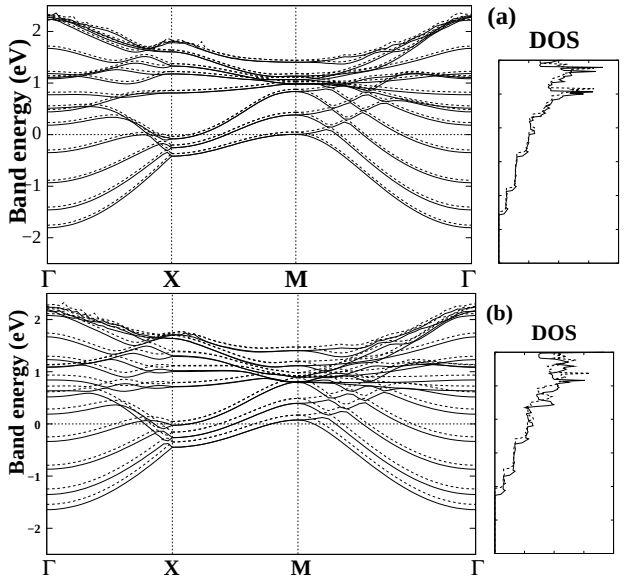

FIG. 1: Band structure and electronic DOS for a 6 layer Cs film: (a) LSDA, and (b) GGA results. Bands are plotted along lines joining high symmetry points in the surface BZ of the films, and the Fermi energy has been set to zero. Majority (up) and minority (down) spin bands and DOS are shown with solid and dotted lines respectively.